



# Theoretical and practical energy limitations of organic and ionic liquid-based electrolytes for high voltage electrochemical double layer capacitors

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## HIGHLIGHTS

- Importance of salt concentration for the development of high energy supercapacitors.
- High voltage PC-based electrolytes feature promising properties.
- Ionic liquids-based EDLCs display limited power at room temperature.

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## ABSTRACT

In EDLCs the energy is stored in the double layer formed by the ions of the electrolyte. Hence, during charge–discharge the ion concentration changes and therefore also the electrolyte should be considered as active material. In the past it has been shown that the performance of EDLCs based on non-aqueous electrolytes is mainly limited by ion concentration of the electrolytes. Taking this point into account, we considered the influence of the salt concentration on the theoretical and practical energy of high voltage EDLCs containing innovative electrolytes with the aim to understand the advantages and the limits related to their use.

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## 1. Introduction

Electrochemical double layer capacitors (EDLCs), also known as supercapacitors, are today advancing as one of the most promising energy storage technology [1,2]. In EDLCs the charge is electrostatically stored at the electrode–electrolyte interface and because of this storage mechanism these devices can be charged and discharged within seconds, they feature high power (up to 10 kW kg<sup>-1</sup>) and an extremely high cycle life (>500,000) [3]. Currently, the commercial available EDLCs contain activated carbon as active material and electrolytes based on quaternary ammonium salt dissolved in organic solvents (acetonitrile (ACN) or propylene carbonate (PC)). The operative voltage of these EDLCs is in the range of 2.3–2.7 V [4]. EDLCs are nowadays conveniently used in a large number of applications where rapid charge–discharge capability

and reliability are required [5]. In the last years, they have also been proposed for high power/energy applications such as hybrid and electric vehicles, power quality systems and smart grids [5]. However, in order to be effectively introduced into these new applications, the performance of EDLCs needs to be improved, particularly in terms of specific energy.

The specific energy of EDLCs is defined by the equation  $E = 1/2CU^2$ , where  $C$  and  $U$  are the capacitance and operative voltage of the EDLC, respectively. Hence, the energy density of EDLCs can be improved by increasing the specific capacitance of the electrode material and/or the operative cell voltage. Regarding electrode materials, several carbonaceous materials such as carbon blacks, carbon aerogels or carbon nanotubes have been proposed as alternatives for activated carbons [1,6–9]. All proposed materials feature interesting properties. Nevertheless, when used in composite electrodes (with mass loading higher than 2 mg cm<sup>-2</sup>), the specific capacitance reported for these alternative materials is in the order of 100–150 F g<sup>-1</sup>. Hence, such alternative materials do not outperform significantly activated carbon-based electrodes. Taking

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this point into account, the greatest progress for carbon-based EDLCs can be presently expected from an increase of the operative voltage.

In the last years, many groups worked on the development of alternative electrolytes for high voltage ( $>3$  V) EDLCs. Among the alternative electrolytes proposed so far, ionic liquids (ILs) are currently considered as one of the most promising. Several groups suggested the use of ILs as electrolytes for supercapacitors. These studies showed that IL-based EDLCs with operative voltages of 3.5 V (or even higher) can be realized [10–13]. This high cell voltage leads to a considerable increment of the energy of these devices. However, due to higher viscosities and lower conductivities of the ILs compared to that of ACN and PC-based systems, the power of IL-based EDLCs appears limited, especially at room temperature. In order to improve the power of high voltage EDLCs, the use of electrolytes containing mixtures of organic solvents (PC or ACN) and ILs has also been proposed [14–16]. Depending on the IL/organic solvent ratio, such mixtures can feature high conductivity, low viscosity and wide ESW. Hence, these characteristics enable the development of high performance devices [15,17,18]. In these electrolytes, the ILs simply act as a conducting salt, and it is important to notice that these mixtures can feature much higher salt concentration compared to conventional electrolytes.

Zhang et al. showed that the performance of EDLCs based on non-aqueous electrolytes is mainly limited by ion concentration of the electrolyte [19,20]. For this reason, the use of highly concentrated electrolytes, e.g. mixtures of ILs and organic solvents, appears promising. But even more, the utilization of solvent-free electrolytes, e.g. pure ILs, is desirable for the increment of the energy density of EDLCs. Although the salt concentration appears an aspect of great importance in view of the development of innovative electrolytes, it is interesting to note that a detailed investigation about the influence of this parameter on the energy of EDLCs containing the above mentioned alternative electrolytes has not been carried out, so far.

In this manuscript, we considered the influence of the salt concentration on the theoretical and practical energy of high voltage EDLCs containing pure IL and PC-based electrolytes. Initially, following the approach proposed by Zhang et al., the theoretical influence of the electrolyte on the energy density of EDLCs is considered. Afterwards, the physicochemical characteristics, such as conductivity, viscosity, etc., of 5 non-conventional electrolytes for high voltage EDLCs are compared with those of conventional electrolytes. Finally, the impact of different electrolytes on the theoretical and practical energy limitations of EDLCs is critically discussed.

**Table 1**

Comparison of the water content, ionic conductivity (at 20 °C), viscosity (25 °C) and ESW (at 20 °C, on platinum working electrode, 1 mV s<sup>-1</sup> scan rate, 0.1 mA cm<sup>-2</sup> threshold value) of the considered electrolytes. In the table also the maximum operative voltage and suitable ratio between positive and negative AC electrode for such voltage are also indicated.

Electrolyte	Water content (ppm)	Conductivity (20 °C) / mS cm <sup>-1</sup>	Viscosity (25 °C) / mPa s	ESW (20 °C) / V	Maximum operative voltage in EDLCs / V	Ratio of activated carbon loading on electrodes in EDLCs / m <sup>2</sup> /m <sup>3</sup>
Pyr <sub>14</sub> TFSI	<9	2.2	77.1	5.6	3.7	1.30
Et <sub>3</sub> NHTFSI	<10	4	39	3.8	2.4	0.5
3.8 M Me <sub>3</sub> STFSI in PC	<5	5.4	31	4.8	2.9	1.2
1.5 M Pyr <sub>14</sub> TFSI in PC	<10	10.4	5.6	5.4	3.5	1.3
1.9 M Pyr <sub>14</sub> BF <sub>4</sub> in PC	<24	10.2	6.3	5.5	3.2	1.6
1.0 M Et <sub>4</sub> NBF <sub>4</sub> in PC	<11	14.5	2.5	4.9	2.7	1.0
1.0 M Et <sub>4</sub> NBF <sub>4</sub> in ACN	<7	56.1	0.6	4.0	2.7	1.0

## 2. Experimental

The organic solvents ACN (Sigma–Aldrich, Germany) and PC (UBE, Japan), the conducting salts tetraethylammonium tetrafluoroborate (Et<sub>4</sub>NBF<sub>4</sub>, Sigma–Aldrich, Germany), and N-methyl-N-butyl pyrrolidinium tetrafluoroborate (PYR<sub>14</sub>BF<sub>4</sub>, Iolitec, Germany) are commercially available and were used as received without any further purification.

The ionic liquids tetraethylammonium bis-[(trifluoromethyl)sulfonyl]imide (Et<sub>3</sub>NHTFSI), trimethylsulfonium bis-[(trifluoromethyl)sulfonyl]imide (Me<sub>3</sub>STFSI) and N-methyl-N-butyl pyrrolidinium bis-[(trifluoromethyl)sulfonyl]imide (PYR<sub>14</sub>TFSI) were synthesized according to procedures described in references [21–24].

All electrolytes (expect the solvent-free) were prepared in an argon filled glove box and the concentration of all of them can be found in Table 1. Their water contents were evaluated using an automated Karl-Fischer titrator. As reported in Table 1, all investigated electrolytes contained less than 25 ppm of water.

Composite electrodes containing activated carbon (DLC Super 30, Norit) as the active material were coated on Al foil following the procedure reported in Ref. [9]. The activated carbon is mainly microporous (92% of micropore volume, 0.78 cm<sup>3</sup> g<sup>-1</sup>), has a specific surface area (BET) about 1410 m<sup>2</sup> g<sup>-1</sup> and the oxygen surface functionality is about 4–5% (95% carbon) [25]. The composition of the dry electrodes was 90% of AC, 5% conducting agent (C65, TIMCAL) and 5% sodium carboxymethyl-cellulose binder (CMC, Walocel CRT 2000 PPA 12 from Dow Wolff Cellulosics). The activated carbon loading on the electrodes was in the range of 6 mg per cell, and the electrode area was 1.13 cm<sup>2</sup>. The electrode coating density (referred to the whole electrode mass loading and dry coating thickness) was about 0.5 g cm<sup>-3</sup> for all electrodes.

Electrochemical investigations were carried out with Swagelok®-type cells. The cells were assembled in an Argon-filled glove box with oxygen and water contents lower than 1 ppm. Experiments were carried out using 2-electrode configuration. Whatman GF/D glass microfiber filter of 675 µm in thickness and 12 mm in diameter served as a separator in all experiments. It was drenched with 120 µL of electrolyte solution.

The electrochemical cycling tests were performed at 20 °C (controlled temperature) using a VMP multichannel potentiostatic–galvanostatic system (Biologic Science Instrument, France). Galvanostatic charge–discharge cycling was carried out using current densities ranging from 0.1 to 10 A g<sup>-1</sup>.

Impedance spectra of EDLCs were recorded at controlled temperature of 20 °C using a Solartron model 1260 impedance/gain-phase analyzer with 5 mV alternating current perturbation in the frequency region from 500 kHz to 1 mHz.

The values of capacitance of the total active material ( $C_{\text{tam}}$ ), average energy ( $E_{\text{average}}$ ) and average power ( $P_{\text{average}}$ ) have been calculated, if not further specified, as indicated by the following formulae [9,17].

$$C_{\text{tam}} = \frac{I\Delta t}{\Delta U m} \quad (1)$$

$$E_{\text{average}} = \frac{I}{m} \int U dt_{\text{discharge}} \quad (2)$$

$$P_{\text{average}} = \frac{E_{\text{average}}}{t_{\text{discharge}}} \quad (3)$$

In these equations,  $I$  is the set current (in A),  $U$  is the voltage (in V),  $t$  is the time (in s) and  $m$  is the total electrode loading of two electrodes (in g).

### 3. Results and discussion

#### 3.1. Electrolyte as active material

Usually, only the electrode material is considered as active material in electrochemical energy storage devices. Energy, power and capacitance are often referred to the electrode loading only. However, in EDLCs the energy is stored in the double layer formed by the ions of the electrolyte and therefore the electrolyte should be considered as active material, as well. Zheng et al. considered this aspect and reported on the limitations of energy density for electrochemical capacitors [19,20]. According to their work, the energy density of an EDLC based on the electrode material (capacitance of one electrode) can be expressed by Equation (4).

$$E = \frac{1}{8} C_{\text{electrode}} U^2 \quad (4)$$

$C_{\text{electrode}}$  and  $U$  are the specific capacitance of the electrode material and the operative cell voltage of the EDLC, respectively.

The maximum energy density based on the electrolyte can be expressed by Equation (5).

$$E_{\text{electrolyte}} = \frac{1}{2} Q U = \frac{1}{2} \alpha c_0 F U \quad (5)$$

$Q$  is the free ionic charge density in the electrolyte,  $c_0$  is the salt concentration of the electrolyte (mole per unit weight or volume) and  $F$  is Faraday's constant (96.4853365 C mol<sup>-1</sup>).  $\alpha$  is a dimensionless constant, which is lower than 1, and represents the fraction of total salt removed from the bulk electrolyte upon complete charging.  $\alpha$  depends on mainly two factors, namely the degree of dissociation of salt molecules and the conductivity of the electrolyte. For instance, for most aqueous electrolytes the dissociation degree is almost 1, meaning that nearly all molecules are dissociated. On the contrary, for non-aqueous electrolytes and pure ionic liquids the number of free ions decreases due to ion pair formation [26]. Thus, the free ion concentration is always lower than the salt concentration. Furthermore, the charging process of a capacitor leads to a reduction of free ions in the bulk electrolyte, leading to an increase of the electrolyte resistance.

Theoretically, in an optimized EDLC the maximum capacitance delivered by the electrode should be equal to that of the electrolyte. Therefore, the electrolyte should just contain the amount of ions needed to match the capacitance of the activated carbon electrode.

In this optimized design, the maximum energy density ( $E$ ) based on the electrode ( $E_{\text{electrode}}$ ) and electrolyte ( $E_{\text{electrolyte}}$ ) can be calculated by Equation (6).

$$\frac{1}{E} = \frac{1}{E_{\text{electrode}}} + \frac{1}{E_{\text{electrolyte}}} \quad (6)$$

By substituting Equations (4) and (5) into Equation (6), the maximum theoretical energy density of an EDLC can be obtained, as described by Equation (7).

$$E = \frac{1}{8} C_{\text{electrode}} U^2 \frac{1}{1 + \frac{C_{\text{electrode}} U}{4 \alpha c_0 F}} \quad (7)$$

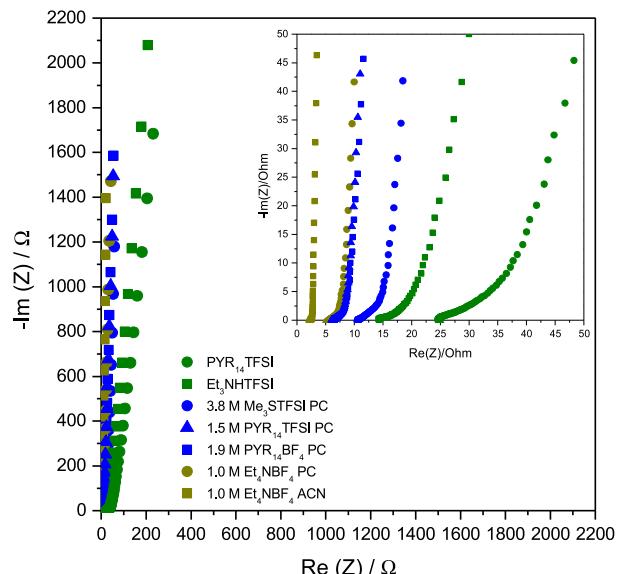
Equation (7) provides the possibility to calculate both maximum gravimetric (Wh kg<sup>-1</sup>) and volumetric energy density (Wh L<sup>-1</sup>). For the maximum gravimetric energy density,  $C_{\text{electrode}}$  is the capacitance per unit weight and  $c_0$  is the electrolyte concentration per unit weight of the salt and solvent combined. In approximation,  $\alpha$  is assumed to be 0.5 for non-aqueous electrolytes and ionic liquids. This means when the EDLC is fully charged, half of the salt concentration in the bulk electrolyte is used to charge the capacitor.

It is well known that the energy density of EDLCs is limited by the specific capacitance of the electrode and the operative cell voltage. Nevertheless, Zheng et al. showed that in organic-based EDLCs the ion concentration of the electrolyte is limiting the energy density of the devices even more than the two above mentioned parameters. Taking this point into account, advanced EDLCs should therefore contain electrolytes with high ion concentration and high electrochemical stability.

The charge accumulated in an EDLC cell is proportional to the cell voltage, cell capacitance (two electrodes) and total electrode loading ( $m_{\text{cell}}$ ). It can be expressed by Equation (8).

$$Q_{\text{cell}} = m_{\text{cell}} C_{\text{cell}} U_{\text{cell}} \quad (8)$$

In a symmetric cell, both electrodes are balanced and also equal the charge of ions consumed from the electrolyte (optimum design). The maximum charge from ions available in the electrolyte can be expressed according to Equation (9).



**Fig. 1.** Impedance spectra of EDLCs containing the electrolytes considered in this work. The spectra were recorded prior to the cycling procedure at controlled temperature of 20 °C.

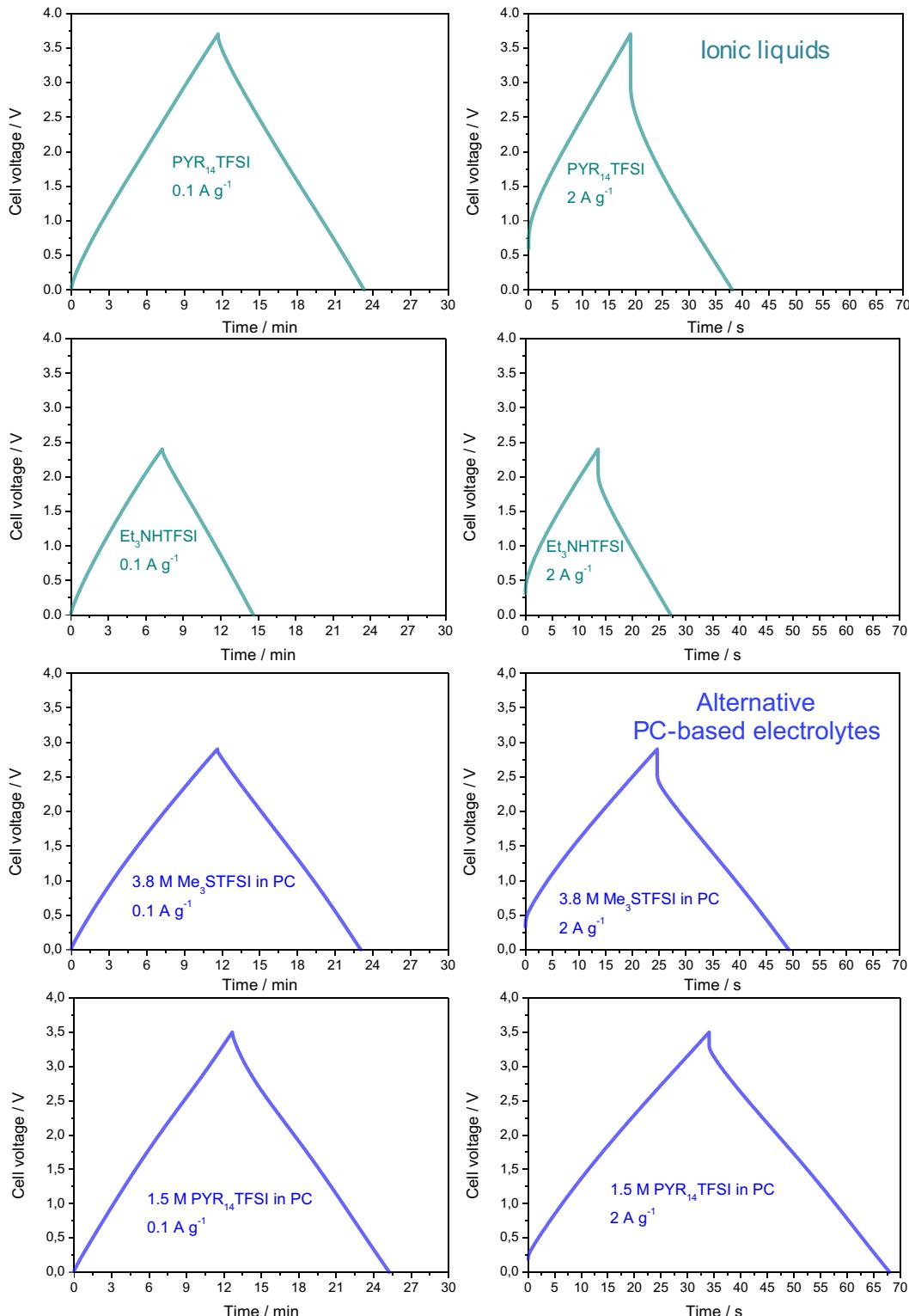
$$Q_{\text{electrolyte}} = \frac{m_{\text{electrolyte}} c_0 F}{\rho} \quad (9)$$

$\rho$  is the density of the electrolyte.

In an optimized (ideal) design, the charge of the electrolyte is equal to the charge delivered by the EDLC electrodes and therefore

$Q_{\text{cell}} = Q_{\text{electrolyte}}$ . Taking this point into account, and combining Equations (8) and (9), the minimum amount of electrolyte can be calculated according to Equation (10).

$$m_{\text{electrolyte}} = \frac{m_{\text{cell}} C_{\text{cell}} U_{\text{cell}} \rho}{c_0 F} \quad (10)$$



**Fig. 2.** Voltage profiles of EDLCs containing the electrolytes considered in this work during charge–discharge test carried out at low ( $0.1 \text{ A g}^{-1}$ , left) and high ( $2 \text{ A g}^{-1}$ , right) current density (both current densities values refer to the total AC loading of the cell).

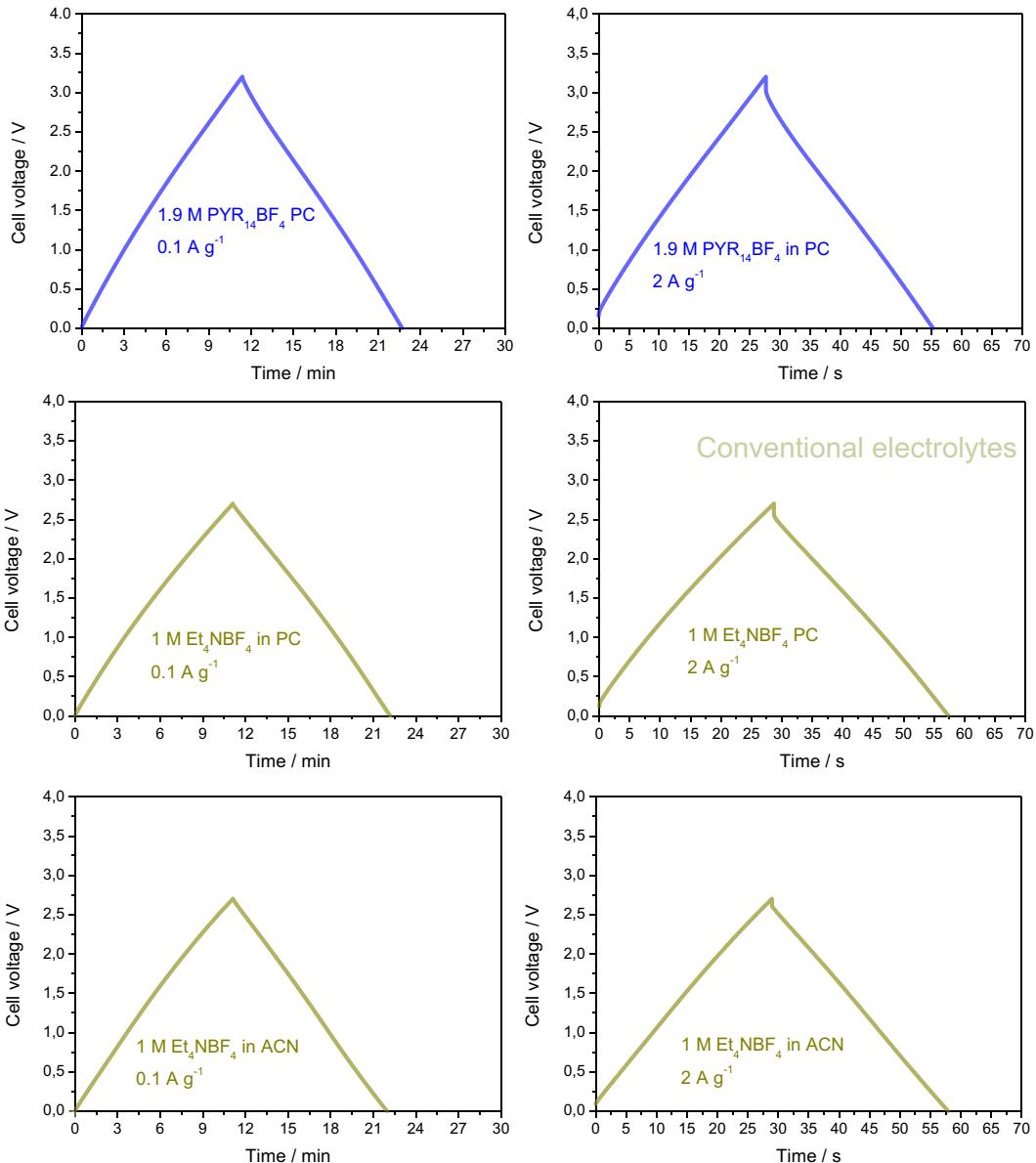


Fig. 2. (continued).

Using this expression, the minimum amount of electrolyte theoretically necessary for the realization of an optimized cell configuration can be easily calculated. Nevertheless, it is important to consider the fact that in EDLCs the electrolyte must be used in excess (e.g. stored in the separator). Therefore, from the practical point of view such an amount does not appear realistic. Nevertheless, such values are of interest because they might give indications about the influence of the salt concentration on the amount of requested electrolyte as well as on the energy density of EDLCs.

### 3.2. Non-conventional electrolytes for EDLCs

With the aim to investigate the influence of the electrolytes on the theoretical and practical energy of EDLCs, five non-conventional electrolytes were selected and compared with conventional organic electrolytes. The considered electrolytes can be divided in three categories: solvent-free (pure ILs), alternative solvent-based electrolytes and conventional solvent-based

electrolytes. Two ILs, the aprotic ionic liquid (PYR<sub>14</sub>TFSI [27]) and the protic ionic liquid (Et<sub>3</sub>NHTFSI [28]), were selected as solvent-free electrolytes. In the case of the alternative solvent-based electrolytes, three PC-based electrolytes were chosen: 1.5 M PYR<sub>14</sub>TFSI in PC [17], 3.8 M Me<sub>3</sub>STFSI in PC [29] and 1.9 M PYR<sub>14</sub>BF<sub>4</sub> in PC [30]. The first of these alternative electrolytes contains a mixture of a room temperature IL with PC, the second a mixture of a non-room temperature IL with PC and the third a mixture of a conducting salt with PC. As conventional electrolytes, 1 M Et<sub>4</sub>NBF<sub>4</sub> in ACN and 1 M Et<sub>4</sub>NBF<sub>4</sub> in PC were utilized for comparison.

**Table 1** compares several properties of the electrolytes, including water content, conductivity, viscosity, electrochemical stability window (ESW) and maximum operative voltage. As shown, all electrolytes have water content lower than 25 ppm. Therefore, they can be considered as suitable for an use in EDLCs. The ACN-based electrolyte features the highest conductivity (56.1 mS cm<sup>-1</sup>). This value is considerably higher than those exhibited by the other electrolytes. Especially, the pure ILs have noticeably lower conductivities of less than 4 mS cm<sup>-1</sup>. The PC-

based electrolytes (conventional and non-conventional) exhibit conductivities ranging from 5.4 to 14.5 mS cm<sup>-1</sup>. The viscosity of solvent-free electrolytes is the highest, while that of the ACN-based electrolyte is the lowest among the investigated electrolytes. As expected from the conductivity, the PC-based electrolytes feature viscosity in between those of ACN and pure ILs.

$\text{PYR}_{14}\text{TFSI}$  has the largest, while  $\text{Et}_3\text{NHTFSI}$  the smallest ESW on platinum electrodes among the considered electrolytes. This difference is due to the presence of the proton on the cation  $\text{Et}_3\text{NH}^+$ , which limits the stability against reduction of this cation. As visible, the ESW of all PC-based electrolytes (conventional and non-conventional) is larger than that of the ACN-based one. In the case of the PC-based electrolytes, it is interesting to mention that the anions  $\text{BF}_4^-$  and  $\text{TFSI}^-$  display comparable stability against oxidation [17,28,29]. However, the stability against reduction for the considered cations is rather different and follows the trend  $\text{PYR}_{14}^+ > \text{Et}_4\text{N}^+ > \text{Me}_3\text{S}^+ > \text{Et}_3\text{NH}^+$  [12,17,28,29]. This different cathodic stability is mainly responsible for the different ESWs observed for the PC-based electrolytes.

As shown, for all electrolytes the operative voltage is significantly lower than the estimated ESW. This difference, as already reported, is caused by the fact that oxidation and reduction reactions of the electrolytes are catalysed by the high surface area activated carbon. Concerning the maximum operative voltage, it should be noted that all EDLCs can be cycled at the indicated operative voltage at least for 60,000 cycles showing capacitance retention of 80%, or higher, during tests carried out at current densities of 1–2 A g<sup>-1</sup> (per total activated carbon loading in the cell) [12,17,27–30].

Several works outlined the importance of an adequate electrode balancing for the realization of high voltage EDLCs with stable performance [12,17,25,28,29,31]. Taking this point into account, Table 1 also gives an indication about the most suitable electrode ratio ( $m_+/m_-$ ), which has been calculated considering the positive and negative potential limits defined during cyclic voltammetry experiments [12,17,25,28,29,31].

In order to develop high voltage supercapacitors, the ability of the used electrolytes to prevent anodic dissolution of the Al current collector of the positive electrode has to be considered [28,29,32]. Several studies showed that the anion  $\text{BF}_4^-$  is able to prevent anodic dissolution of Al and can be safely used in EDLCs. On the contrary, the anion  $\text{TFSI}^-$  might not feature such ability [29,32,33]. Nevertheless, it has been shown that all TFSI-based electrolytes considered in this work are able to prevent anodic dissolution of Al [5,17,28–30]. From this point of view, all electrolytes considered in this work appear suitable for an application in high voltage EDLCs.

### 3.3. Theoretical and practical energy limitations of non-conventional electrolytes for EDLCs

Fig. 1 compares the impedance spectra of all electrolytes investigated in this work. The influence of electrolyte viscosity-conductivity can be clearly seen. Specifically, the EDLCs that contain highly viscous and pure ionic liquids differ more strongly from the ideal shape (vertical line) of the Nyquist plot profile compared to solvent-based systems. Moreover, the IL-based EDLCs exhibit an increased resistance as indicated by the increase of the real part of the impedance. As expected, the EDLC containing the most conductive and less viscous electrolyte, namely 1.0 M  $\text{Et}_4\text{NBF}_4$  ACN, features almost the ideal Nyquist plot profile and the lowest resistance.

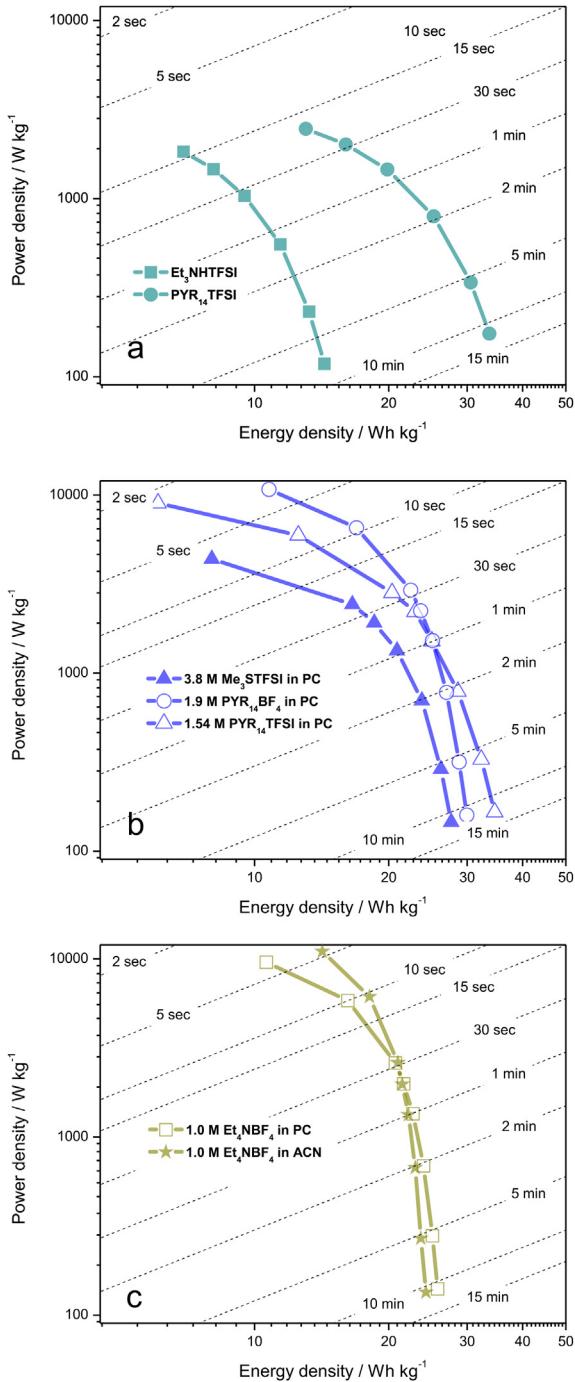
Fig. 2 compares the voltage profiles of EDLCs containing all electrolytes considered in this work. The voltage profiles were recorded at relatively low (0.1 A g<sup>-1</sup>) and relatively high (and 2 A g<sup>-1</sup>)

current density in order to evaluate the influence of this parameter on the operative voltage, ohmic drop (and thus ESR) and capacitance of the EDLCs. As shown, at low current densities the resistance of all EDLCs is rather small and thus the applied and the real operative voltage are rather similar for each EDLC. On the contrary, at high current density the ohmic drop and thus ESR has a stronger influence on the voltage profile, limiting the performance of higher viscous electrolytes. As reported in the previous section, the conductivity of the solvent-free electrolytes is about 10–15 times lower compared to the conventional ACN electrolyte. Consequently, at high current density the ohmic drop observed in devices containing these electrolytes is relatively high, and the real operative voltage is lower than the applied one (see Fig. 2). For instance, when a current density of 2 A g<sup>-1</sup> is applied, the EDLC containing  $\text{PYR}_{14}\text{TFSI}$ , which has an operative voltage of 3.5 V, has a real voltage of 3.11 V. This difference corresponds to a decrease of 11%. At the same current density, the decrease between applied and real voltage for the ACN-based EDLC is only of 3%. It is interesting to note that the difference between the applied and the real operative voltage of conventional and the alternative PC-based EDLCs is not very marked. For example, the electrolyte 1.9 M  $\text{PYR}_{14}\text{BF}_4$  in PC shows a difference between the applied and the real operative voltage of 5%. This value is similar to that shown by the conventional electrolyte 1 M  $\text{Et}_4\text{NBF}_4$  in PC (4%). In order to compare the energy and the power of EDLCs containing different types of electrolytes and having different operative voltages, the different behaviour of these devices at high current densities needs be considered. Taking these differences into account, the use of the applied maximum operative voltage for the calculation of the energy's device might be misleading. Therefore, the use of average energy and power (see experimental section) should be always preferred for such a comparison.

Fig. 3 compares the average energy and power density of EDLCs containing the investigated electrolytes in a Ragone-like plot. The tests were carried out at 20 °C and the operative voltage applied to each device was the one as indicated in Table 1. It is important to notice that all EDLCs were assembled using the same AC and all of them had a comparable mass loading. To make a comparison easier, the figure is divided in three parts: solvent-free electrolytes (Fig. 3a); alternative solvent-based electrolytes (Fig. 3b) and conventional solvent-based electrolytes (Fig. 3c). As shown, when low current densities are applied the beneficial effect on the use of a high operative voltage is clearly visible. The EDLCs with an operative voltage of 3.5 V feature the highest energy. On the contrary, the EDLC containing the protic ionic liquid  $\text{Et}_3\text{NHTFSI}$  exhibits the lowest performance because of its low operative voltage (2.4 V). When high current densities are applied, the ACN-based EDLC shows the highest power due to the highest conductivity. Nevertheless, it is interesting to notice that the EDLCs containing the alternative PC-based electrolytes show promising performance, as well. Particularly, the device with 1.9 M  $\text{PYR}_{14}\text{BF}_4$  in PC features higher energy and power than the one with the conventional PC-based electrolyte at all considered current densities.

As mentioned in the previous paragraph (*Electrolyte as active material*), the performance of EDLCs in terms of energy and power is usually referred to the electrode loading only. Although this method is commonly used in the literature, this calculation underestimates the role of the electrolyte which is actively participating to the charge-discharge process of these devices. The energy density of EDLCs depends on the amount of ions in the electrolyte, as well. Moreover, the higher the ion concentration of the electrolyte the higher will be the energy density of the device, as less electrolyte is needed to match the capacitance of the electrode material.

With the aim to understand the influence of the concentration of the investigated electrolytes on the energy density of EDLCs,

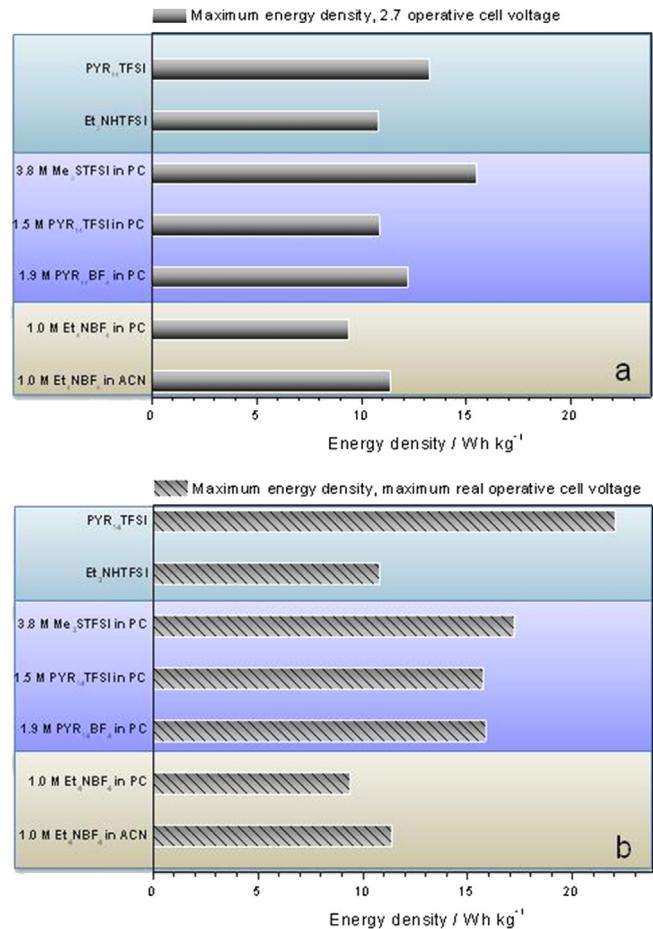


**Fig. 3.** Ragone-like plots of EDLCs containing the electrolytes considered in this work. The average values of energy and power density refer to the total AC loading in the cell. For this comparison current densities between 0.1 and 10 A g<sup>-1</sup> (per total AC loading in the cell) were applied at 20 °C. Some of the more viscous electrolytes could be only used at lower current densities. Times shown are the time constants of the EDLCs obtained by dividing the energy density by the power.

Equation (7) was applied to calculate the theoretical maximum gravimetric energy of all devices. For the parameter  $\alpha$ , a value of 0.5 was selected. As mentioned above, this value can be considered as a reasonable approximation for non-aqueous electrolytes and ionic liquids as those used in this study [19,20,34–37]. It is important to notice that all other parameters present in this equation were obtained experimentally. In order to have a better insight on the influence of the ion concentration, two voltage values were used for

the calculation of the theoretical maximum gravimetric energy for each electrolyte: the maximum, effective (considering the ohmic drop) operative voltage obtained from the test carried out at 0.1 A g<sup>-1</sup> (see Fig. 1a) and 2.7 V (except for Et<sub>3</sub>NHTFSI where a value of 2.39 V was used due to the limited electrochemical stability of this electrolyte).

As shown in Fig. 4a, which refers to the calculation made using an operative voltage of 2.7 V, the energy density of an EDLC depends strongly on the salt concentration. The EDLC containing the electrolyte 3.8 M Me<sub>3</sub>STFSI in PC, which is the one having the highest ion concentration among the investigated devices, features much higher energy density (about 1.7 times) than that of the EDLCs containing the conventional electrolytes. These results clearly confirm the indication of Zheng et al. about the important contribution of ion concentration on the EDLC's energy. When the maximum achievable operative voltage is used for the calculation, the operative voltage has a significant influence on the energy density (Fig. 4b), as well. The (solvent-free) PYR<sub>14</sub>TFSI-based EDLC, which features the highest operative voltage (3.67 V) and high ion concentration (estimated in the order of 3.3 M), is the device with the highest energy density. Nevertheless, it is very interesting to point out that when the maximum operative voltage is considered, the ion concentration affects dramatically the energy density, as well. As shown, among the EDLCs containing the three alternative



**Fig. 4.** Maximum theoretical energy densities of EDLCs the electrolytes considered in this work calculated for devices with operative voltage of 2.7 V as well as for devices with displaying the maximum operative voltage achievable with the used electrolyte (expect for EDLCs containing Et<sub>3</sub>NHTFSI where a voltage of 2.39 V was considered). The comparison has been made considering current density of 0.1 A g<sup>-1</sup> (per total AC loading in the cell) and a value of  $\alpha = 0.5$  was used for all electrolytes.

**Table 2**

Maximum real voltage, electrode capacitance, theoretical maximum energy density of EDLCs containing the investigated electrolytes. The numbers in brackets are the energy density calculated based on the EDLC AC loading only. The theoretical minimum amount of electrolyte per total AC loading is also included.

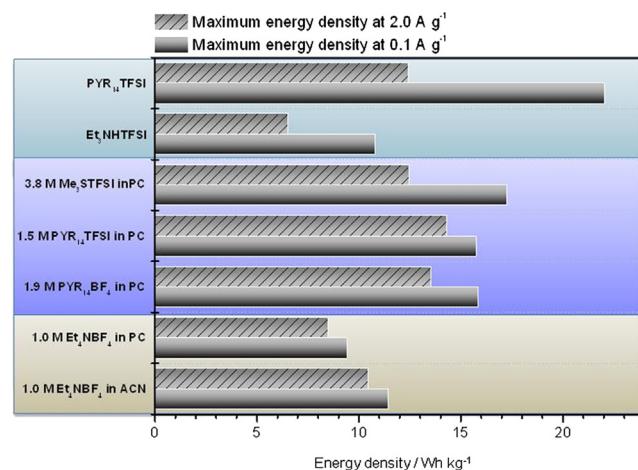
Electrolyte	Maximum real voltage / V	Electrode capacitance / F g <sup>-1</sup>	Theoretical maximum energy density / Wh kg <sup>-1</sup>	Theoretical minimum amount of electrolyte m <sub>electrolyte</sub> / m <sub>AC-cell</sub>
Pyr <sub>14</sub> TFSI	3.67	76	22.05 (35.5)	0.31
Et <sub>3</sub> NHTFSI	2.39	73	10.8 (14.56)	0.17
3.8 M Me <sub>3</sub> STFSI in PC	2.88	95	17.25 (27.37)	0.29
1.5 M Pyr <sub>14</sub> TFSI in PC	3.49	86	15.77 (36.54)	0.65
1.9 M Pyr <sub>14</sub> BF <sub>4</sub> in PC	3.19	85	15.86 (30.08)	0.45
1.0 M Et <sub>4</sub> NBF <sub>4</sub> in ACN	2.7	96	11.42 (24.42)	0.57
1.0 M Et <sub>4</sub> NBF <sub>4</sub> in PC	2.7	98	9.4 (24.94)	0.82

PC-based electrolytes, the one with 3.8 M Me<sub>3</sub>STFSI in PC exhibits higher theoretical energy than the devices containing 1.9 M PYR<sub>14</sub>BF<sub>4</sub> in PC and 1.5 M PYR<sub>14</sub>TFSI in PC, although these latter systems have much higher operative voltages. The higher theoretical energy is obviously originated by the higher ion concentration of the former electrolyte confirming the beneficial effect of highly concentrated electrolytes on the EDLC's energy.

**Table 2** compares several parameters of the investigated EDLCs. Among them, the maximum operative voltages as experimentally observed during tests at 0.1 A g<sup>-1</sup> (**Fig. 1a**) are given. In order to have an indication about the influence of the conductivity-viscosity of the electrolyte on electrode capacitance, the capacitance shown by the AC electrodes in each electrolyte is reported, as well. As shown, the specific capacitance of the AC is about 70 and 100 F g<sup>-1</sup>. Many studies investigated the influence of the electrolyte properties, e.g. conductivity, viscosity and ion size, on the specific capacitance of activated carbons [15,18,38–43]. These results confirm that the capacitance of electrodes containing the same material might change significantly when different electrolytes are used. The table also includes the theoretical maximum gravimetric energy density (calculated using Equation (7)) of the investigated EDLCs as obtained considering the maximum operative voltage of each electrolyte. For comparison, the energy density based on the electrode mass loading only is also included in **Table 2** (in brackets). Hence, the different contributions to the energy density by the electrolyte and electrode loading are directly visible. Additionally, the theoretical minimum amount of electrolyte necessary for each EDLC (calculated according to Equation (10)) is given in the table. About this latter point, it is interesting to notice that high concentrated electrolytes, such as 3.8 M Me<sub>3</sub>STFSI in PC and ionic liquids, theoretically require significant lower amounts of electrolyte. This reduced amount of electrolyte would reduce the weight of the device, and it could theoretically contribute to increased energy densities. However, in commercial cells the electrolyte has always to be used in excess. An amount of about 2.5 times larger than the minimum theoretically required is typically used. Therefore, even if theoretically advantageous, it has to be proved if a reduced amount of electrolyte will be sufficient for the cell and does not reduce its performance.

In order to have an indication about the influence of the current densities, the energy delivered by the EDLCs at high current was also calculated. The two current densities considered above

(0.1 A g<sup>-1</sup> and 2 A g<sup>-1</sup>) were used for the comparison. In the case of the low current (0.1 A g<sup>-1</sup>), the EDLCs are charged–discharged between 11 and 13 min, while at 2 A g<sup>-1</sup> only 19–29 s are needed. As shown in **Fig. 5**, the EDLCs containing alternative PC-based electrolytes feature good energy densities at high current density, due to the higher conductivity of such mixtures. By contrast, the pure ionic liquid based devices lose large parts of their energy (e.g. 1.8 times less energy for PYR<sub>14</sub>TFSI at high current density). Interestingly, due to high salt/ionic liquid concentration all electrolytes (except Et<sub>3</sub>NHTFSI) feature higher theoretical energy densities with respect to the commercial electrolytes. The most promising electrolytes appear to be highly concentrated PC-based mixtures, e.g. 1.9 M PYR<sub>14</sub>BF<sub>4</sub> in PC, due to the best compromise in terms of energy and power. It is interesting to notice that PYR<sub>14</sub>BF<sub>4</sub> is a salt and can be dissolved up to concentrations of 3 M in PC. Such high concentration could further increase the energy of the EDLC. However, it would most likely decrease the power of the device because the viscosity will be increased [30].



**Fig. 5.** Comparison of the maximum theoretical energy densities of EDLCs the electrolytes considered in this work at low (0.1 A g<sup>-1</sup>) and high (2 A g<sup>-1</sup>) current density (both current densities values refer to the total AC loading of the cell). The comparison has been made considering a value of  $\alpha = 0.5$  for all electrolytes, using the maximum real operative voltage achievable with each electrolyte.

## 4. Conclusions

In this manuscript, we considered the influence of the salt concentration on the theoretical and practical energy of high voltage EDLCs containing pure IL and PC-based electrolytes. Usually, the energy density of EDLCs refers only to the electrode loading. Although commonly used in the literature, this calculation underestimates the role of the electrolyte which is actively participating to the charge–discharge process of these devices. The energy density of EDLCs is also depending on the amount of ions in the electrolyte. The higher the ion concentration the higher will be the energy density. Additionally, in order to achieve high energy, the electrolyte needs to have a large electrochemical stability as the energy depends on the operative voltage. One of the key factors for the realization of next generation EDLCs appears to be the development of electrolytes with a wide practical operative voltage (higher than 2.7 V) and high salt concentration. The results of these studies indicate the electrolytes 1.9 M PYR<sub>14</sub>BF<sub>4</sub> in PC and 3.8 M Me<sub>3</sub>STFSI in PC as promising candidates for the realization of advanced EDLCs. Both of them exhibit high ion concentration (higher than 1.5 M), acceptable conductivity (ca. 5–10 mS cm<sup>-1</sup> at 20 °C) and high operative voltage. Hence, such innovative electrolytes enable the development of EDLCs with higher energy compared to systems containing conventional ACN and PC-based electrolytes.

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